

## Potential of Fluorescent Polymer as Sensing Reagent in Optical Fibre Sensor

Rusli Daik, Musa Ahmad, Leong Yung Ta and Ooi Hoe Peng

School of Chemical Sciences and Food Technology  
Faculty of Science and Technology, Universiti Kebangsaan Malaysia  
43600 Bangi, Selangor

**Abstract:** Poly(4,4'-diphenylene diphenylvinylene) was prepared from an aromatic diketone compound, namely 4,4'-dibenzoylbiphenyl via the McMurry condensation reaction using  $\text{TiCl}_4$  as the catalyst with zinc dust as the reducing agent. Preliminary results on fluorescence and UV-Visible absorption spectroscopies showed that the polymer is highly fluorescent and responsive to the presence of oxygen gas.

**Abstrak:** Poli(4,4'-difenilena difenilvinilena) telah disediakan daripada satu sebatian dwiketon aromatik, iaitu 4,4'-dibenzoilbifenil melalui tindak balas gandingan McMurry dengan menggunakan  $\text{TiCl}_4$  sebagai mangkin bersama serbuk zink sebagai agen penurunan. Hasil pencirian asas terhadap polimer yang dihasilkan menggunakan spektroskopi pendaflour dan UL-Nampak menunjukkan polimer mempunyai keamatan pendaflour yang tinggi dan responsif terhadap kehadiran gas oksigen.

Received 2.4.01; accepted 2.1.02

### Introduction

Poly(arylene vinylene)s, PAV, are of special interest in the field of materials for solid-state electronics [1,2,3]. They are attractive materials since they can be solution-processed using a range of well-established techniques, and also a large variety of structures can be generated using techniques of synthetic organic chemistry. The use of such materials in device configuration has been demonstrated, for instance, in light emitting diodes (LEDs) [4,5], batteries [6] and as well as in sensors [7]. Advantages of such polymers in sensor development being the possibility of combining the necessary properties of the materials, such as conductance and fluorescence, and outstanding physical characteristics of the materials, such as thermal stability, relatively inert to moisture, mechanical strength and solubility in common organic solvents. Researches in the area of sensing generally, and specifically on optical fibre based sensor, are growing rapidly and still in its infancy [8]. Advantages of optical fibre based sensors as compared to the conventional counterparts include free from interference of electromagnetic radiation, rust-proof, allowing the real time monitoring, flexible, robust and relatively cheap [9]. Most of researches on application of PAV as the sensing reagent in optical fibre sensor are based on either conductivity or redox potential of the material [10]. However, the exploitation of the unique property of PAV, which is fluorescence, is not widely reported. The application of fluorescent simple compounds and inorganic complexes in optical fibre sensor was reported, however, problems such as low solubility, stability and fluorescence brightness retarded the development of the sensors [10]. In this paper we report our attempt to discover the possibility of using a PAV type polymer, namely poly(4,4'-diphenylene diphenylvinylene), PDPV, as a sensing reagent in optical fibre sensor which is

based on the fluorescence property of the polymer. The polymer was prepared from an aromatic diketone compound, namely 4,4'-dibenzoylbiphenyl via the McMurry condensation reaction using  $\text{TiCl}_4$  and Zinc dust as the catalyst and reducing agent respectively. Preliminary results on UV-visible and fluorescence spectroscopies of the polymer are discussed.

### Experimental

#### Monomer synthesis

Benzoylchloride (27 mL, in excess) was added to biphenyl (6.0 g, 0.04 mole) in a three neck round bottom flask (250 mL) equipped with a magnetic stirring bar, a condenser and a thermometer under dry nitrogen atmosphere. The mixture was stirred and cooled to below  $10^\circ\text{C}$  in an ice-bath. Anhydrous iron(III)chloride (41.4 g, 0.25 mole) was slowly added to the mixture over a period of about 30 minutes. The mixture was then stirred at room temperature for another 30 minutes followed by heating at  $80^\circ\text{C}$  for 4 hours. At room temperature, the mixture was added to ice-water (500 mL) while stirring. The suspended white solid was collected, washed with KOH (5%) and water until the washings were neutral. The product was dried and recrystallised from toluene (3 times) to give a pure 4,4'-dibenzoylbiphenyl compound.

#### Polymer synthesis

Zinc dust (0.94 g, 0.014 mole) was added to THF in a three neck round bottom flask (250 mL) fitted with a condenser, a magnetic stirring bar and a thermometer under dry nitrogen atmosphere. Titanium tetrachloride (1.30 mL, 0.012 mole) was then added to the mixture at about  $0^\circ\text{C}$ . The mixture was stirred at room temperature for 30 minutes and then refluxed for about an hour. After adding 4,4'-dibenzoylbiphenyl (0.65 g, 0.002

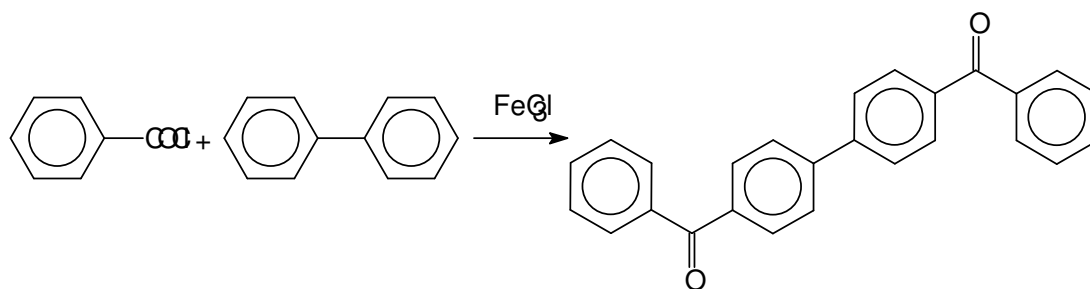


Figure 1. Synthesis of 4,4'-dibenzoylbiphenyl

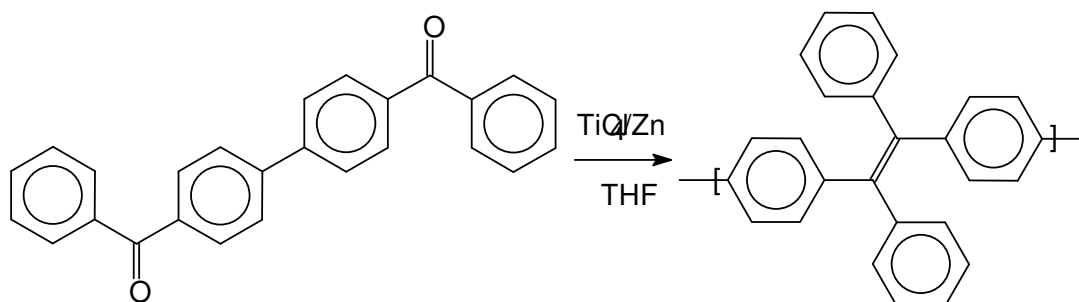


Figure 2. Synthesis of PDPV

mole) at room temperature, the mixture was further refluxed for 20 hours. At about 0°C, HCl (80 mL, 2 M) was added to the mixture and the product was extracted into chloroform (30 x 50 mL). The combined extracts were washed with saturated solution of NaCl, dried over anhydrous MgSO<sub>4</sub> and the solvent was evaporated to give a concentrated polymer solution. The polymer was then reprecipitated into methanol to give a yellowish green granule of PDPV.

## Results and discussion

### *Synthesis and characterisation of 4,4'-dibenzoylbiphenyl and PDPV*

Elemental, spectroscopic and thermal analyses of 4,4'-dibenzoylbiphenyl and PDPV showed that the products were the desired compounds and was reported elsewhere [11]. The number average molecular weight found for PDPV was 50,000 as measured by gel permeation chromatography on chloroform solution of the polymer using polystyrene as the standard.

### *UV-visible spectroscopy*

The UV-Visible absorption spectrum was recorded for chloroform solution of the polymer. The spectrum obtained for PDPV showed main peaks at 264 nm and 342 nm. The strong absorption peak at 264 nm can be attributed to the secondary absorption band of delocalised electrons within pendant benzene ring and the peak at 342 nm indicated the presence of conjugation sequence along the PDPV backbone chain. From the edge of the spectrum, we found a band gap of the polymer of about 2.80 eV, indicating that the polymer produced may have characteristics of a semiconductor [10].

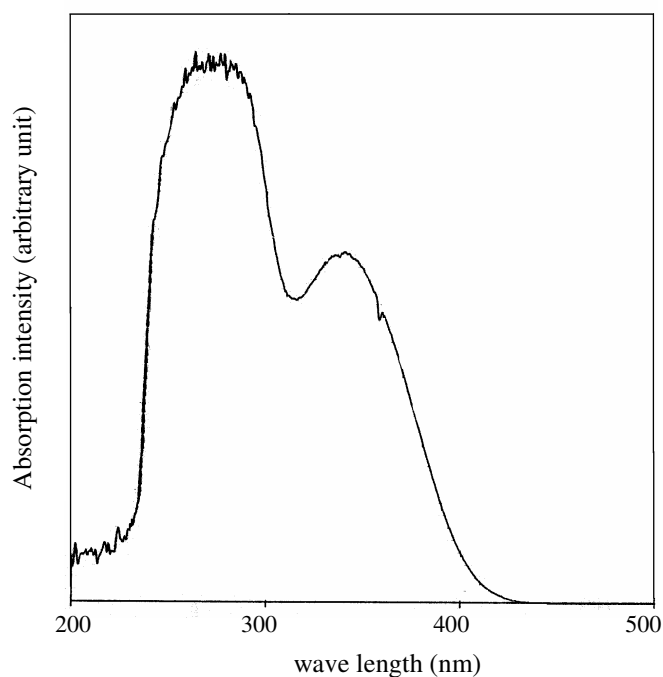


Figure 3. UV-Visible absorption spectrum of PDPV

### *Excitation and fluorescence spectroscopy*

The excitation spectrum obtained for PDPV did not show a clear mirror image to the respective fluorescence spectrum, however, the absorption peak at lowest energy (495 nm) is close enough to the peak at highest energy (497 nm) in the respective fluorescence spectrum. Therefore it is reasonable to conclude that the spectrum obtained was in fact the excitation spectrum for PDPV.

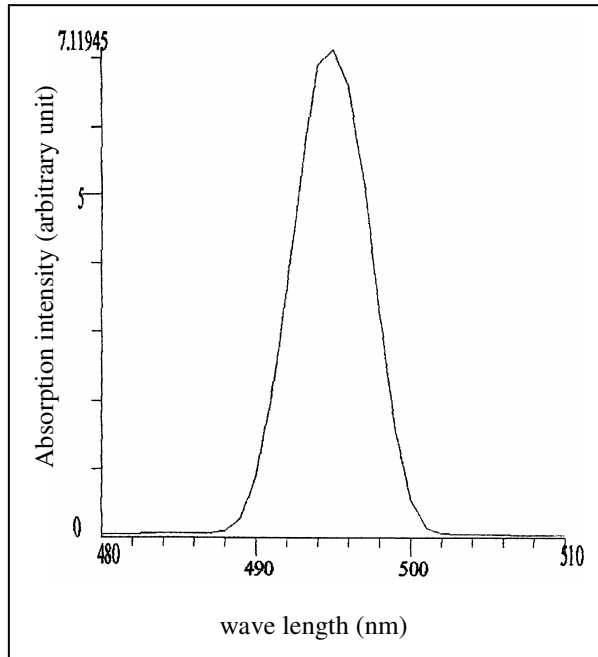


Figure 4. Excitation spectrum of PDPV

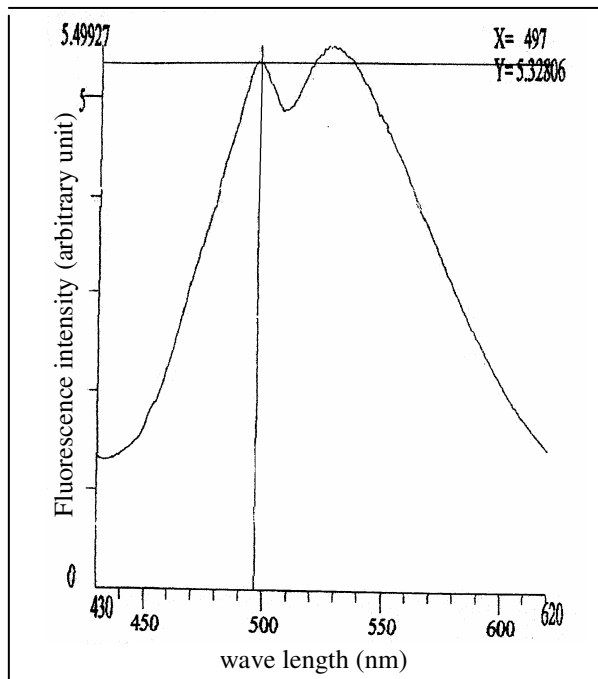


Figure 5. Fluorescence spectrum of PDPV

#### The effects of oxygen gas on fluorescence

The spectra obtained showed that the fluorescence intensity decreased when the polymer was exposed to continuous flow of oxygen gas as expected. Oxygen gas is known as a good quencher and the proposed mechanism for the quenching process of the fluorescent PDPV with the presence of oxygen gas was presented in Figure 7. It was also found that the fluorescence intensity dropped dramatically at the initial stage before it became almost constant. The explanation would be the rate of quenching process is high at the

initial stage due to the abundant availability of fluorescent PDPV segments.

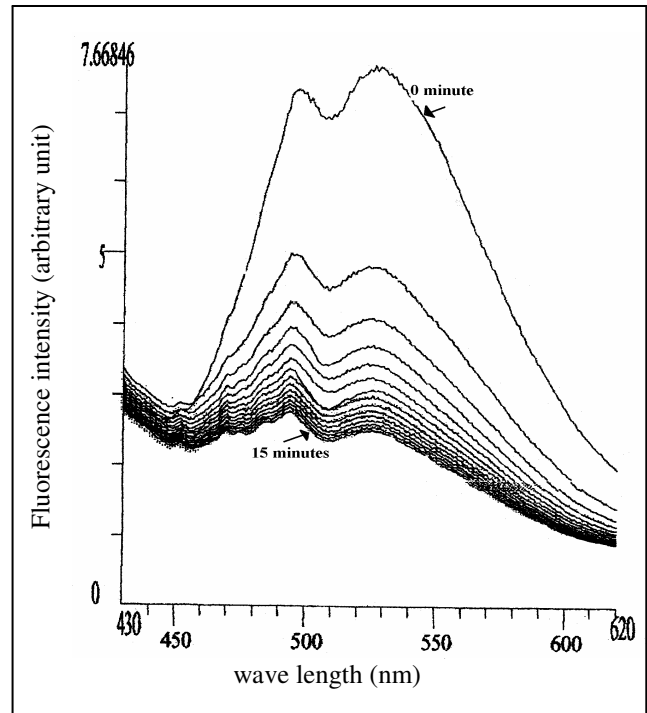


Figure 6. Fluorescence spectra of PDPV when exposed to oxygen gas

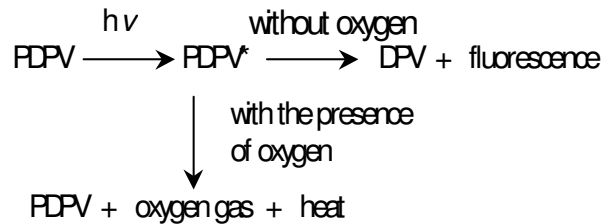
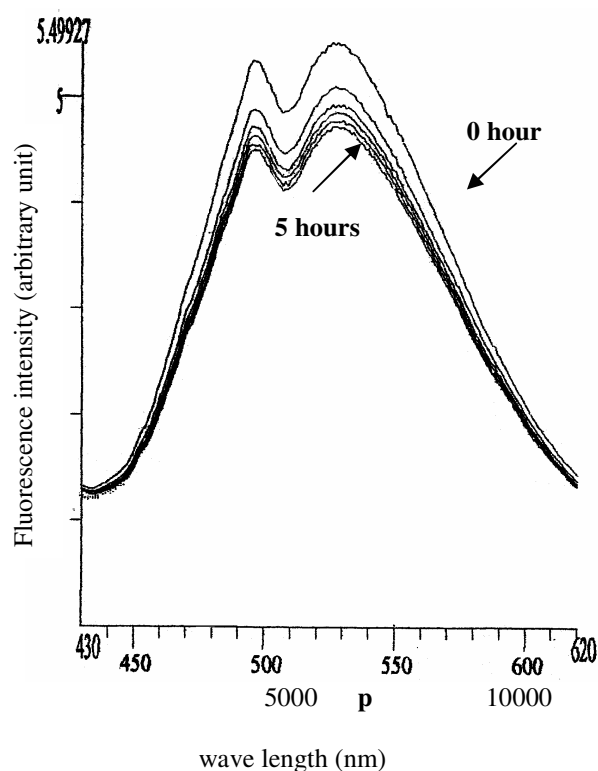


Figure 7. The proposed mechanism for quenching process of the fluorescent PDPV

#### Studies on regeneration of fluorescent PDPV

In this experiment, the regeneration of fluorescent PDPV was attempted by flushing the oxygen-exposed PDPV with nitrogen gas and it is expected that the PDPV with high fluorescence intensity would be re-produced. However, the fluorescence spectra obtained did not show the expected results, instead, the reverse effect was observed. Although, the decrease in fluorescence intensity was almost negligible as compared to the case in which the polymer is exposed to oxygen gas. This observation showed that the PDPV is either very sensitive to the presence of oxygen gas or it is not stable when exposed to the spectrophotometer light source used in this experiment. This matter and other aspects will be pursued by characterising the polymer further.



**Figure 8. Fluorescence spectra of PDPV-oxygen complex when exposed to nitrogen gas**

#### Conclusion

It has been shown that PDPV is potentially useful as a sensing reagent in optical fibre sensor, especially for the detection of oxygen gas. This is due to PDPV is highly fluorescent and responsive to the presence of oxygen gas.

#### Acknowledgement

Authors would like to acknowledge the financial support provided by Malaysia Toray

Science Foundation (1998 Toray Research Grant Award).

#### References

1. Gigli, G., Cingolani, R., Barbarella, G., Favaretto, L., and Cacialli, F. (1999) *Applied Physics Letters*, **75**, 439.
2. Kobayashi, H., Kanbe, S., Kigchi, F.I., Kimura, M., Yusadaka, I., Miyashita, S., Shimuda, T., Towns, C.R., Burroughes, J.H., and Friend, R.H. (2000) *Synthetic Metals*, **111-112**, 125-128.
3. Feast, W.J., Tsiboukklis, J., Pouwer, K.L., Groenendaal, L., and Meijer, E.W. (1996) *Polymer*, **37**, 5017-5047.
4. Zhang, C., Seggern, H.V., Pakbaz, K., Kraabel, B., Schmidt, H.W., and Heeger, A.J. (1994) *Synthetic Metals*, **62**, 35-40.
5. Burroughes, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., Mackay, K., Friend, R.H., Burns, P.L., and Holmes, A.B. (1990) *Nature*, **347**, 539-541.
6. Otero, T.F., and Cantero. (1999) *Synthetic Metals*, **81-82**, 838-841.
7. Holzer, L., Winkler, B., Wenz, F.P., Tasch, S., Dai, L., Mau, W.H., and Leising, G. (1999) *Synthetic Metals*, **100**, 71-77.
8. Musa Ahmad, Harun Hamzah, and Elya Sufliza Marsom (1998) *Malaysia Journal of Analytical Sciences*, **4**, 179-184.
9. Norris, J.O.W. (1989) *Analyst*, **114**, 1359-1372.
10. Hari Singh Nalwa, "Handbook of Organic Conductive Molecules and Polymer" John Wiley & Sons, London (1997), 621-631.
11. Rusli Daik, and W.J. Feast (2000) *Journal of the Institute of Materials Malaysia*, **1(2)**, 31 - 42.